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An Investigation into the Use of Blue Copper Pigments in European Early Printed Books

ABSTRACT

Deterioration of cellulose apparently caused by blue copper pigments was observed in a collection of European early printed books. In a limited survey of these materials, discoloration indicative of deterioration of cellulose was found in half of the examples which contained blue painted initials. Results using false color infrared photography supported the preliminary identification of the blue pigment as copper-based in every instance, including those examples in sound condition. Accelerated aging of fabricated azurite samples prepared in various traditional media showed some discoloration of cellulose with use of tawed goatskin glue, glair, and parchment size. There was no discoloration with a gelatin medium. The most discoloration was observed with the use of gum arabic. A factor in this result may be the known tendency of acidic polysaccharides to sequester heavy metals. More extensive analysis was undertaken of a single severely-degraded historic example, using ultraviolet light, false color infrared photography, scanning electron microscopy with energy-dispersive X-ray spectroscopy, and Fourier transform infrared spectroscopy. The blue pigment was identified as natural azurite, probably in a gum-glair medium, which had been applied over a surface prepared by selectively brushing the paper with an alum wash. Aging tests of various consolidants and mending materials were used to help determine a treatment plan for the single extremely degraded item. Another acidic polysaccharide, funori, predictably showed poor aging characteristics when applied as a consolidant to azurite pigment in these tests.

1. INTRODUCTION

This study was undertaken to examine the use of azurite pigment in European incunabula and the related deterioration observed in one collection. A detailed analysis of a single example showing extreme degradation of the paper support was carried out. Behavior of azurite in various traditional media was considered, and observations from simple tests of possible treatments of azurite on paper were used to determine a treatment plan for a single, severely deteriorated item.

Incunabula are a source of numerous examples of blue pigment on paper, due to the demand for color in books of the fifteenth century. In this period texts were densely formatted within defined areas on the page, and the inclusion of color was important for indicating divisions such as paragraphs and chapter headings. As books began to be produced by printing this appearance of the written page did not immediately change, and color retained its significance. Rubrication[1] of printed books was not done through a desire to imitate the appearance of contemporary manuscripts, but rather because coloring was a part of the way information was conveyed, and hand application was the most efficient way of achieving this available to the early printers (Smith 1994). The complexity of the task of printing in colors (and presumably its expense) can be imagined through viewing the lavish work of Fust and Schöffer in the *Mainz Psalter* and the *Canon Missae* (fig. 1). Studies of the extant copies of the *Mainz Psalter*, for example, have suggested that the “292 metal-cut initials and their arabesque backgrounds had to be picked out of the form and inked separately for each impression” (Levarie 1995).

With the growth of the new technology of printing in Europe, manuscript decoration communities established themselves in printing centers, where the same individuals might work on both printed books and manuscripts (Febvre and Martin 1976). These decorators might be working for the printers and dealers or might be independently employed. The most elaborately-finished works featured illumination and decorated borders, while other copies of the same edition might be sold and later bound completely undecorated. Books were sometimes pur-

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Fig. 1. Two-color printed initials (red and blue). *Canon Missae,* Mainz, Johann Fust and Peter Schöffer, 1458. 39 x 26 cm. Rare Book and Manuscript Library, Columbia University, Goff M736, detail, F2v.

Fig. 2. Bartolomaeus Anglicus. *De Proprietatibus Rerum.* Nuremberg, Anton Koberger, 20 June 1492. 29.3 x 20.3 cm. Archives and Special Collections, Health Sciences Library, Columbia University Medical Center, (uncat.) fol. a1r.

chased as undecorated sheets and decorated to the specifications of the individual buyers. For this reason, the decoration and binding of incunabula has been shown to have frequently taken place in completely different locations from the place of printing.

Koberger's Anglicus of 1492

When Bartholomaeus Anglicus' *De Proprietatibus Rerum* (Nuremberg, Anton Koberger, 1492) arrived in the Columbia University Libraries' conservation laboratory in preparation for a loan, severe deterioration of the paper support was found in all of the areas where initial letters had been applied with blue pigment (fig. 2). The paper on the verso of each initial was dark brown and cracked, with frequent losses in these areas (figs. 3–4).

The Anglicus has a large illuminated first initial and hand-applied red and blue initials throughout the text. Examination of various works printed by Anton Koberger revealed other volumes from the 1480s and 1490s with illuminated first initials which appear to be the work of the same decorator[2] (fig. 5). This finding is a strong indication that the decoration of the Anglicus, including the problematic blue initials, would have been completed at the point of sale in Nuremberg. During examination under visible light, the paper of the Anglicus shows areas of brown discoloration but no embrittlement apart from the pigmented areas. Under magnification the paint layer is a coarse-grained blue, dotted with the occasional green crystal, suggesting that azurite is the pigment used.

Azurite

Azurite is the name used for the mineral, blue basic copper carbonate, which was one of two important blue colorants in the Middle Ages. It often occurs naturally in combination with the more common green copper carbonate, malachite, and may contain malachite impurities (Gettens and Fitzhugh 1993). In Europe during the fifteenth century azurite was considered expensive, but was less costly than ultramarine and therefore might be expected to be used more frequently in a routine application such as rubrication. Because of its lower cost it was often employed as an underpaint for ultramarine in both easel paintings (Gettens and Fitzhugh 1993) and manuscripts

Fig. 3. Blue initial. Bartolomaeus Anglicus. *De Proprietatibus Rerum.* Nuremburg: Anton Koberger, 1492. 29.3 x 20.3 cm. Archives and Special Collections, Health Sciences Library, Columbia University Medical Center (uncat.), detail, fol. a1v.

Fig. 4. Verso, blue initial of figure 3.

(Porter 2003). Studies in the literature provide several examples of azurite's conversion to other products due to environmental influences, including conversion to copper acetate in the presence of formaldehyde (Koseto 1999), to copper chloride when exposed to chlorinated water (Dei 1998), and to the green basic copper carbonate, malachite, with humid storage (Banik 1989). Azurite blackens in warm alkalis (Gettens and Fitzhugh 1993).

As a cheaper alternative to natural azurite, artificial blue copper pigments were produced in the Middle Ages and were significant in the fifteenth century. The products of these recipes have been studied in some depth by several researchers (Orna et al. 1980; Lombardi et al. 2000; Scott 2002). The tests conducted in this study will only consider the behavior of natural azurite, but the possibility remains that some of the historical examples examined here actually contain artificial copper blues.

Survey of Selected Incunabula

Although the Anglicus was not immediately available for further study, investigations into the problem began with an examination of other incunabula in the collections at Columbia. Several examples of discoloration related to cellulose degradation in the presence of blue pigment were identified (fig. 6). One volume printed by Nicolaus Jenson exhibited damage similar in magnitude to the Anglicus. There was no noticeable embrittlement, but disfiguring clouds of brown discoloration were seen on recto and verso surrounding each blue initial (fig. 7).

A more systematic survey of all of Columbia's books printed by Jenson and Koberger was undertaken involving a total of thirty-four volumes spanning the period from 1470 to 1498. The survey found 44% of these examples incorporated blue color and, of those, 53% exhibited discoloration of the paper support on the verso of the blue

Fig. 5. Angelus de Clavasio, *Summa Angelica de Casibus Conscientiae.* Nuremberg, Anton Koberger, 10 February 1492. 30.7 x 20.2 cm. Rare Book and Manuscript Library, Columbia University, Goff A722, fol.a1r.

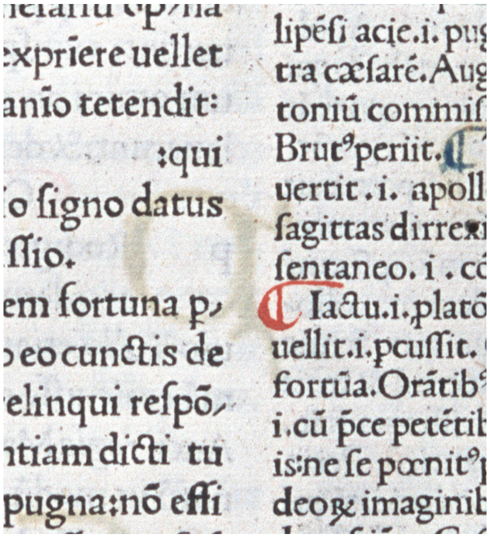

Fig. 6. Verso of blue initial "P." Valerius Maximus, *Facta et Dicta Memorabilia.* Venice: Joannes Gregoriis de Forlivio et Socii, 18 June 1482. 30.7 x 20.7 cm. Rare Book and Manuscript Library, Columbia University, Goff V33, detail, fol. a8[v].

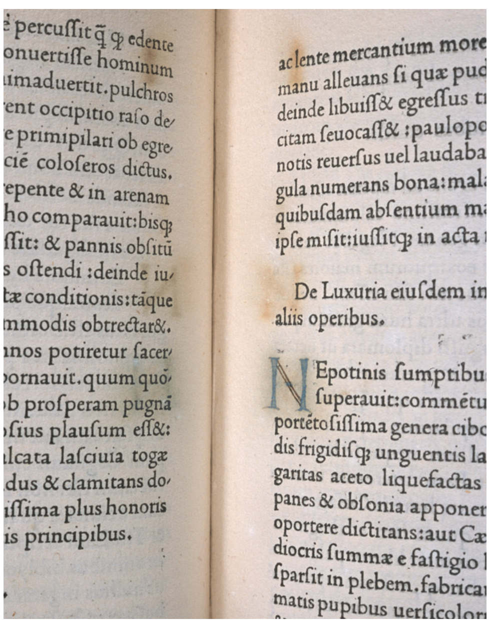

Fig. 7. Recto and verso of several blue initials, showing cloud-like discoloration. Suetonius, *Vitae XII Caesarum.* [Venice], Nicolaus Jenson, 1471. 28.7 x 18.9 cm. Rare Book and Manuscript Library, Columbia University, Goff S817, detail, fols. 86[v]–87[r].

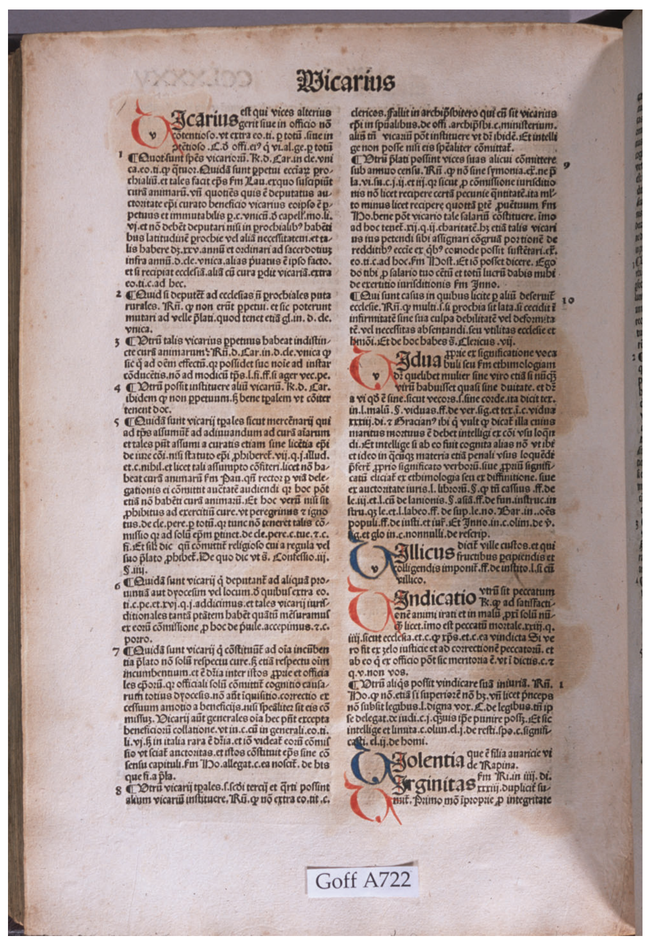

Fig. 8. Brown staining, probably a surface preparation applied by the decorator. Angelus de Clavasio, *Summa Angelica de Casibus Conscientiae.* Nuremburg: Anton Koberger, 10 February 1492. 29.3 x 20.3 cm. Goff A722. Rare Book and Manuscript Library, Columbia University, fol. 285[v].

pigmented areas. One work (fig. 8) showed squares of brown staining of the paper where most of the initials had been applied, probably caused by a surface preparation of the paper by the decorator. Increased discoloration of the paper support relating to the blue initials was seen in these areas. (This work, printed by Koberger in the same year as the Anglicus, was one of those whose illuminated initials closely matched it. Therefore it most likely passed through the same workshop for at least some of its decoration, but the hand of the individual who applied the painted initials is different.)

Another frequent observation during the survey was blackening of the paper support beneath the blue initials (fig.9), which was not counted as cellulose deterioration. In addition, the paint layer of six of the blues appeared darkened and was cracked in some cases. Instances of this blackening phenomenon have been observed since at least the fifteenth century, when the "Bolognese Ms." (Ms. 1536, Biblioteca Universitaria di Bologna) warned about its occurrence in liquid mixtures of azurite with gum arabic or glair (Merrifield 1975, 410). This blackening was duplicated by mixing ground azurite with gum arabic solution. A watery gray component separated out upon standing, which darkened to black upon drying. When the

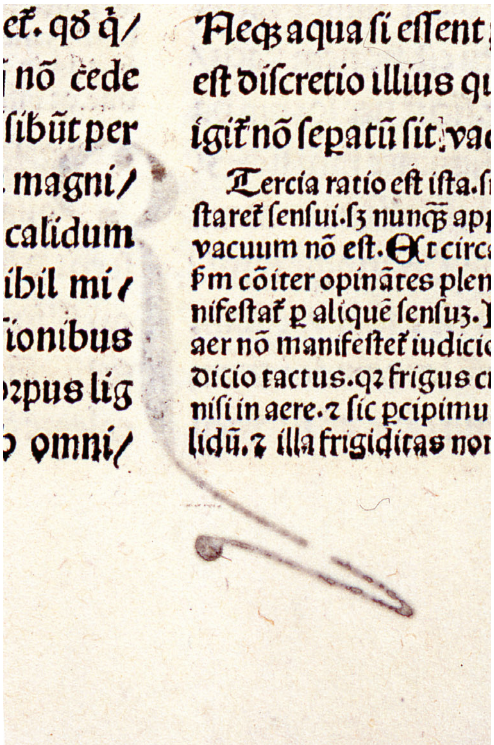

Fig. 9. Blackened paper support, verso of blue initial "Q". Lambertus de Monte, *Copulata […] Super Octo Libros Phisicorum Aristotelis.* Cologne, Heinrich Quentell, [14]93. 28.5 x 19.5 cm. Rare Book and Manuscript Library, Columbia University, Goff M833, detail, fol. 75v.

solution was applied to unsized paper this component migrated noticeably to the verso of the support (fig. 10). The black products of these reactions have not been identified, although azurite's ability to convert to black copper compounds has been documented (Gutscher et al. 1989).

II. AZURITE ON PAPER AND IN TRADITIONAL

Copper Pigments on Paper

The ability of copper to degrade cellulose is well-established. Copper (I) or Copper (II) ions can catalyze oxidation through free-radical reactions, which also can lead to simultaneous hydrolysis of cellulose. These reactions can initiate in both acidic and alkaline environments (Banik 1982). Concentrations of copper in paper have been shown to increase over time as the ions diffused from a malachite paint layer in one study (Hoshi and Kitada 2002).

While it is acknowledged that copper pigments as a group can be damaging to paper, studies in the conservation literature have usually focused on green copper pigments. The chapter on media problems of the *Paper Conservation Catalog* describes the copper-catalyzed deterioration associated with copper greens, in particular verdigris and copper resinate. Azurite is listed as being subject to discoloration due to environmental factors (Ash et al. 1985). Fuchs and Oltrogge report observing azurite-induced damage "very frequently," and attribute it to the addition of ammonium chloride as a color enhancer, which reacts with copper, forming the cuprammonium ion and dissolving cellulose (1992, 32). Banik reports that "only few cases are known in which azurite causes paper to decompose" (1989, 61). He explains that verdigris, copper acetate, is more destructive to paper than the copper carbonates because it is more water-soluble and so more easily absorbed by cellulose. The mechanism for copper carbonate-induced damage is the reaction of sulfur dioxide and humidity converting the basic copper carbonate "to a more soluble basic copper sulfate that then accelerates the decomposition of the support material" (Banik 1989, 69–70).

This attribution of the damage to the formation of copper sulfates is compelling, since the two notable instances of azurite-related damage in the literature both implicate exposure to alum, potassium aluminum sulfate. A study of azurite and malachite staining in Japanese panel paintings concludes that this staining was caused by the deterioration of the *dosa* [animal glue and alum sizing] and pigments (Emoto 1979). Another study, involving azurite in deteriorated areas of hand-colored Dutch atlases, also identifies alum which was present as a surface preparation of the paper (Tsai 1992). Both of these studies also report frequent observation of damage caused by azurite.

Azurite in Traditional Media

The discovery in the incunabula survey of a group of examples of what appear to be blue copper pigments, some of which have caused discoloration of cellulose, raises the question of how particular components of the paint mixtures could influence the occurrence of deterioration. Reference to historic painting treatises reveals two fifteenth-century works which give specific instructions for selecting media for blue pigments. One of these, the

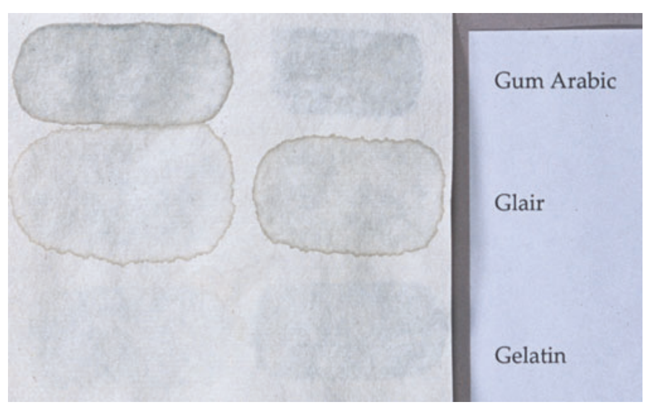

Fig. 10. Verso, azurite in gum Arabic compared with other media, unsized paper, unaged sample.

Bolognese Ms., instructs the reader to mix blue pigment with "size made from clippings of white chamois leather and it will be good" (Merrifield 1975, 408). In modern terminology "chamois" refers to oil-tanned leather; however in medieval usage the term "connoted a soft, supple material" (Reed 1972). "White chamois leather" may be defined as alum-tawed skin with reasonable certainty: a contemporary manuscript contains the instruction to make glue from "the white leather of which gloves are made" (Ms. Latin 6741, Bibliotèque Nationale de Paris, translated in Merrifield 1975, 262). Used as a binding medium with azurite, a glue made from this skin would present one way for alum to enter the paint mixture. None of the fifteenth-century texts were found to contain specific instructions for preparing paper as a painting surface, but two seventeenth-century treatises (*Book of Drawing* 1652; Salmon 1672) both instruct the reader to brush alum water on paper as a surface preparation, "…for that keeps the colors from sinking into the paper…" (Salmon 1672, 212–213). In general recommendations for manuscript painting, gum arabic is the most commonly mentioned binding medium for manuscripts, followed by glair. Mixtures of these two are also frequently recommended.

Published studies in the conservation and chemistry literature make some predictions possible about the behavior of azurite in these media. The deterioration of gum arabic caused by copper pigments has been reported in the conservation literature (Fuchs and Oltrogge 1992; Daniels 2002). In the chemistry literature certain studies of the corrosion of metallic copper by gum arabic are perhaps even more enlightening. One such study used real-time Fourier transform infrared spectroscopy (FTIR) to compare the action of different agents and found that gum arabic was the second most effective (after alginic acid) at removing copper from a metal film and incorporating it into its own matrix (Jolley et al. 1989). Gum arabic is a calcium, magnesium, or potassium salt of arabic acid. The ion exchange properties of acidic polysaccharides, notably brown seaweed mucilages, "have been studied in detail and it is well established that bivalent metal ions exchange with counter ions of polysaccharides such as alginic acid (in brown algae)" (Vieira and Volesky 2000, 20). It is interesting to note that reported maximal uptakes of Cu by brown algae occur consistently at pH 4.5 (Davis et al. 2003), while the pH of gum arabic ranges from 4.5–5.5 in aqueous solutions. It is therefore reasonable to expect that mixtures with azurite could bring about chelation of Cu^{2+} ions from the pigment with gum arabic, which, as a highly soluble material, also can act as a vehicle for uptake of copper by the cellulose fibers when in less viscous solutions.

Gelatin's ability to render other bivalent metal ions inert has been documented (Kolbe 2004), and therefore a protective effect with use of pure gelatin could be predicted. Historically, gelatin would have commonly appeared as a binding medium from skin and parchment sources whose contents cannot be precisely known. It would therefore be more difficult to predict the result of these mixtures, although the alum present in tawed skin glue would be expected to have a damaging effect.

III. EXPERIMENTAL

False Color Infrared Photography

Incunabula were photographed using Kodak Ektachrome EIR (35 mm) film with a Wratten Deep Yellow (#12) filter. The light source was daylight temperature strobes (5350±150°K). Two sets of tests were done, one processing the film using E-6 process, and the other using AR-5. A test card of different pigments was photographed. It included examples of azurite, ultramarine, and indigo/woad from multiple sources and mixed with different binders. All of the azurite appeared blue-violet, ultramarine was red or red-violet, and indigo was also red or red-violet and therefore indistinguishable from ultramarine. When azurite samples subjected to accelerated aging were photographed the results were still blue-violet, but in the most degraded examples this was such a dark shade that it appeared nearly black. These results were consistent and reproducible, but differed in specific ways from those obtained in other studies (Hoeniger 1991; Moon et al. 1992; Porter 1997). (Two of these studies also differ from one another in their color results for indigo/woad.) This discrepancy might be due to differences in light sources and filtration used, or possibly to the change made in the film emulsion by Kodak in 1997 (Eastman Kodak Co. 1997), which postdates the sources consulted.

Aging Tests – Preparation of Samples

In all of the aging tests University of Iowa BH (hemp fiber) handmade paper was used, either unsized as purchased, or sized in a bath using a 2% w/v solution of gelatin.

Glair was prepared from egg white by separating it from the yolk, whipping it in a laboratory blender, allowing it to settle, straining it, and then repeating this process. The gelatin, tawed goatskin, and parchment size were prepared in 4.5% w/v aqueous solutions. Gum arabic was prepared in a solution of 20 g gum/100ml water.

Azurite was used as purchased, without further grinding. Paint mixtures were prepared by mixing azurite with the above solutions at a ratio of 1:2 by weight. Application was a single loaded brush stroke. All of the media, without added azurite, were also applied to the sheets. After the paint had dried for two days, the samples were conditioned to 50% RH and sealed in Marvel Seal pouches. To avoid contamination from any residual alum, the tawed skin samples were sealed separately from the rest in all but one of the samples. These were heated to 80°C for 5 and 12 days.

For the testing of consolidants, isinglass, gelatin, and parchment size were all used in 2% w/v aqueous solutions. Klucel G was prepared in the concentration 3 g/100 ml ethanol, and Paraloid B-72 as 3 g/100 ml acetone. Funori was prepared by soaking .25 g in 75 ml H_20, then straining and heating.

For the testing of mending materials, the cooked wheat starch recipe was 40 g starch/280 ml H_20. The cooked paste was strained and diluted to a skim milk consistency, and then brushed onto *usu mino* paper and applied to the sample. Solvent-set tissue was prepared by mixing acrylic resin dispersions (Rhoplex AC73:Rhoplex AC33:H_2O in the ratio 1:1:2) and casting the mixture onto *haini* kozo tissue. It was applied to the sample using ethanol. A 2% w/v mixture of isinglass was cast onto *usu mino* tissue, dried, and applied as a re-moistenable film. Methyl cellulose was applied as a 2.5% w/v aqueous mixture to *usu mino* paper and also used as a re-moistenable film. The sample mends were applied to paint layers of azurite in gum arabic and azurite in glair. To lessen darkening which would obscure the results, the gum arabic solution was prepared in a lower concentration than previously: 12.5 g of gum/100 ml water.

Accelerated aging of the azurite/media samples and consolidants was carried out by Gisela Noack using a Thermoline Hotplate model OV10600 oven. Aging of the mending materials was in a Thelco 70DM mechanical convection oven.

Ultraviolet Light

Examination and photography was performed using a hand-held Blak-Ray model UVL-56 (366 nm) light source.

Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy

The author assisted Dee Breger in carrying out analysis on the LEO 1455 VP scanning electron microscope with attached EDAX energy dispersive X-ray (SEM-EDX) microanalyzer at the Lamont-Doherty Earth Observatory in Palisades, New York. Cross-sectioning of fibers was achieved through immersing the sample in liquid nitrogen and then scoring and breaking it. The samples received two carbon coatings prior to analysis. For the Anglicus analysis, two cross-section samples containing paper and paint were removed from the edges of areas of loss within the Anglicus. The small size of the samples did not permit cross-sectioning of the fibers. An additional sample of paper fibers was removed near a sewing station in the gutter of the same sheet, since this opening offered access to blank fibers for comparison.

Fourier Transform Infrared Spectroscopy

Spectra were collected by the author using the Digilab/Biorad 7000 Fourier transform infrared (FTIR) spectrometer at the Materials Research Science and Engineering Center, Columbia University. Samples were prepared in potassium bromide pellets. The spectrometer was purged for 30 minutes prior to collection to reduce H_2O vapor, and spectra were recorded with a 2 cm^{-1} resolution, collected in 500 scans. The analysis of the spectra was performed by George Tulevski with the author's assistance.

IV. RESULTS AND DISCUSSION

Identification of Blues: False Color Infrared Photography

False color infrared photography was used to determine which of the examples of blue pigment observed in the survey were copper-based. Several studies have documented the procedure for using false color infrared photography for pigment identification, and two of these have particularly noted its ability to distinguish between blue pigments of the medieval period (Hoeniger 1991; Moon et al. 1992; Porter 1997). Twenty-three incunabula containing blue pigment were photographed using this method, including all of the examples identified through the Jenson/Koberger survey. All of the blue pigment, which included the non-flourished initials and paragraph marks as well as more elaborate decoration was shown to be copper-based. This information makes possible a more meaningful interpretation of the results of the survey. Since all of the blue pigment was found to be copper-based, and half of all of the blue in the survey was associated with observed deterioration, this small survey of incunabula identified deterioration of cellulose in the presence of blue copper pigments occurring at a rate of 50%.

Aging Tests of Azurite in Various Media

A series of simple accelerated aging tests was undertaken to compare the behavior of azurite in different mixtures with traditional media (figs. 11–12). One set of solutions mixed medium and pigment in a 2:1 ratio by weight, while the other mixed water:medium:pigment in a 1:1:1 ratio. These were applied to sized and unsized paper. After accelerated aging (figs.13–14), the most degraded samples were the gum arabic/azurite mixtures, followed by glair, and then the tawed size. Parchment size showed slight staining, and gelatin did not show any staining. In those samples made with gum arabic, the paint layer was so degraded that no blue pigment was visible in the sized sample. Where this mixture could better penetrate the paper support in the unsized sample the pigment had survived better, but the paper showed more discoloration. The discoloration

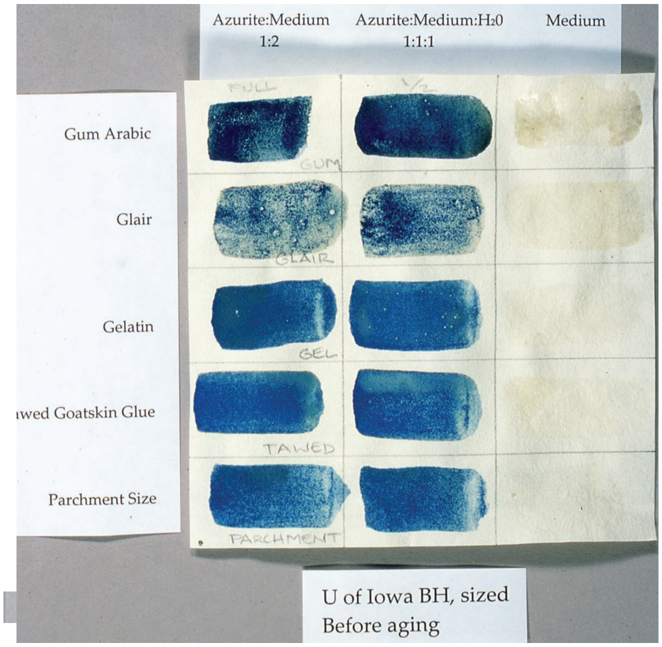

Fig. 11. Recto of azurite sample sheet, unsized paper.

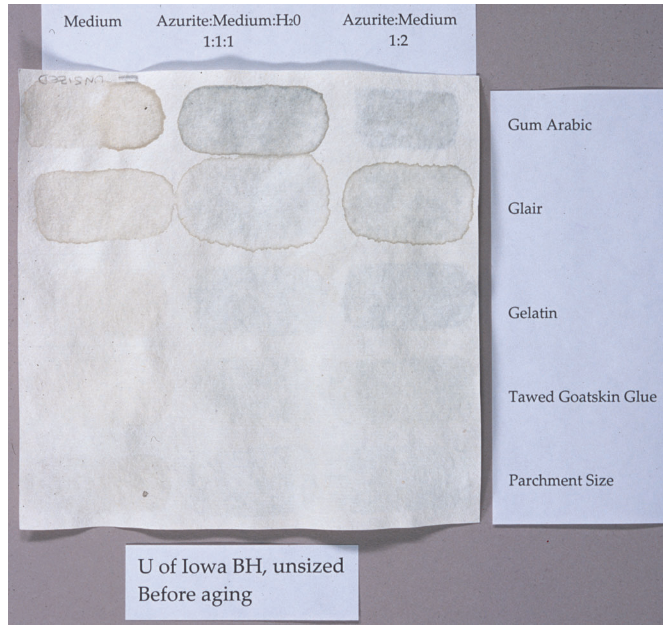

Fig. 12. Verso of azurite sample sheet, unsized paper.

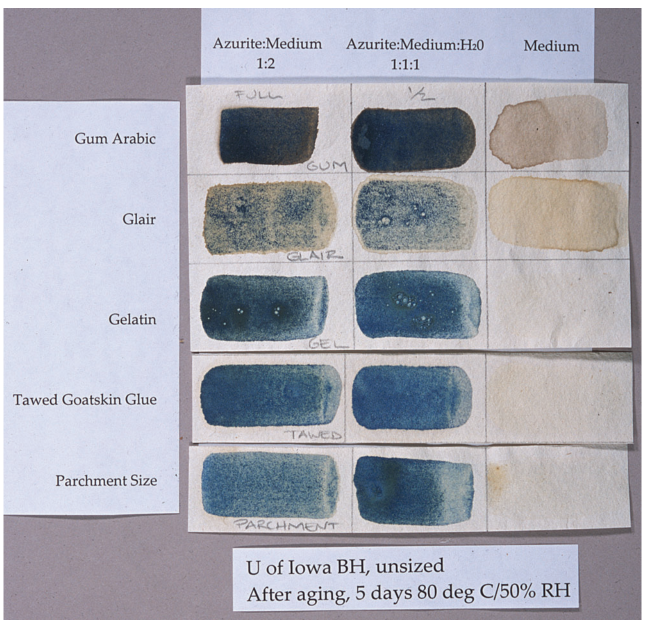

Fig. 13. Unsized sample sheet, verso, after aging 5 days.

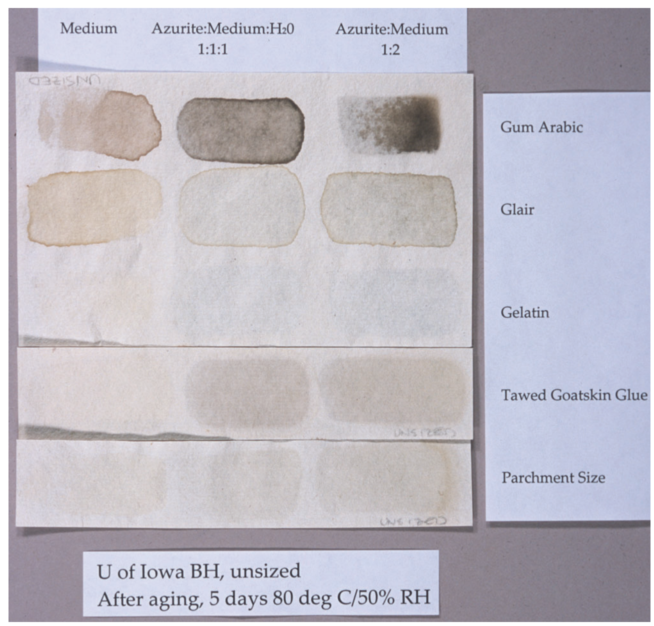

Fig. 14. Sized sample sheet, verso, after aging 5 days.

with a gum arabic medium was noticeably darker than the staining associated with other media, and of a brownish-black color.

The increase of paper discoloration seen in the unsized sheets indicated that the staining in these gum arabic samples was at least partly the visual effect caused by saturation of the paper with the darkened paint mixture. For a better understanding of the condition of the fibers, a 12-day aged sample of azurite in gum arabic on sized paper was examined using SEM-EDX. Examination of a cross-sectioned fiber showed that it contained copper in moderate amounts, which was clustered in small points throughout the fiber (fig. 15).

Anglicus Observations

Ultraviolet light examination showed that many of the brown marks which had been observed on the paper of the Anglicus were in the pattern of large and rather sloppy brush strokes (figs. 16–17). In the sections of the book which required many hand-colored initials, there were

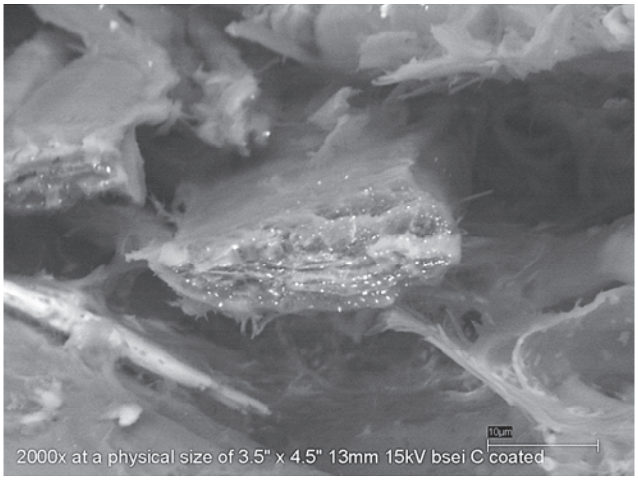

Fig. 15. Scanning electron micrograph. Cross-sectioned hemp fiber from azurite/gum arabic aging test. White spots are areas of high copper content.

three brush strokes per leaf: one for the column of initials on the left side of each page, and one in the center of the leaf which was applied in an area covering the center column of initials on both sides of the leaf. These were obviously applied rapidly, extending in many places into the blank margins of the page, or missing entirely the spaces where they were actually needed. The painted initials frequently extended beyond these areas, and here could be seen a demarcation between damaged and undamaged areas of the initials. Figure 18 shows a blue initial "T" above a red "T" under visible illumination. The line of the revealed brush-stroke is highlighted in this image, and the area covered by the observed substance is to the left of this line. In the UV image (fig. 19), the interaction of the blue paint with the brushed-on substance is clear in the left side of the initial, where the black (presumably high-copper content) areas appear to explode out

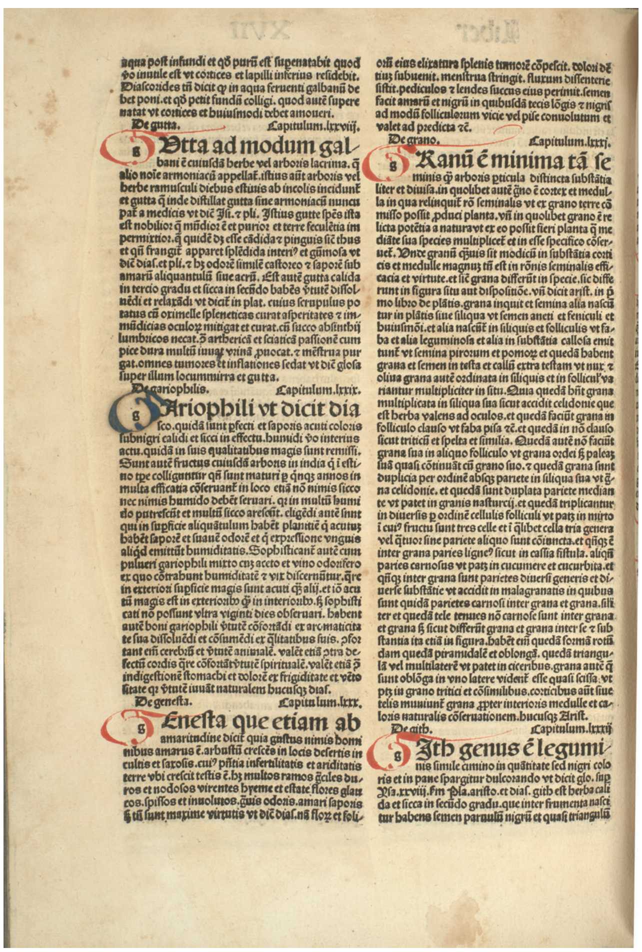

Fig. 16. The middle initial, left column, is blue, while the others are red. Bartolomaeus Anglicus. *De Proprietatibus Rerum.* Nuremberg, Anton Koberger, 20 June 1492. 29.3 x 20.3 cm. Archives and Special Collections, Health Sciences Library, Columbia University Medical Center, (uncat.) fol. y6v. Photograph by Christopher Antkowiak.

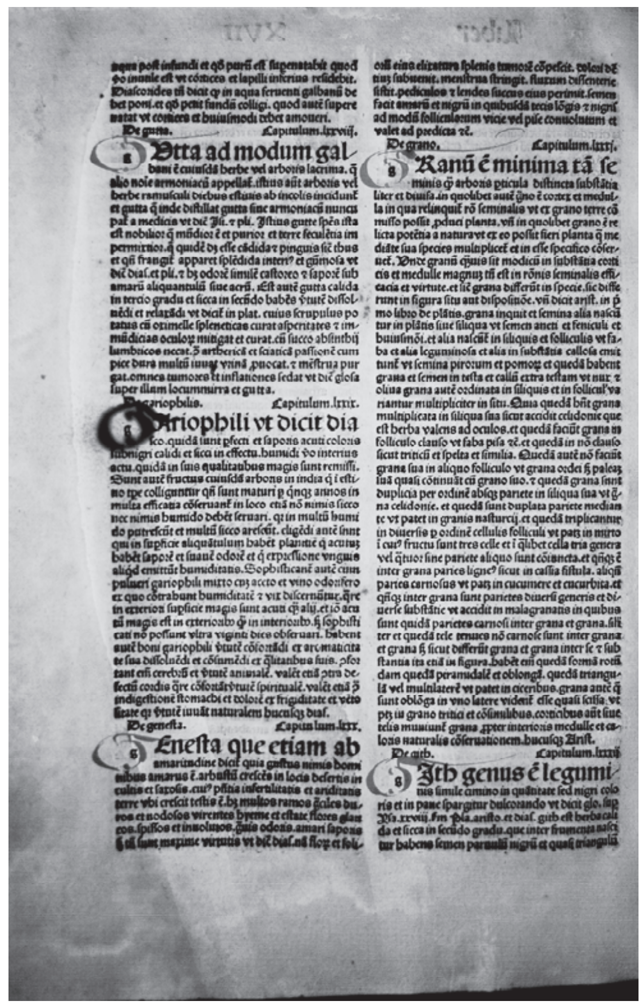

Fig. 17. Anglicus, fol. y6v under UV illumination, showing vertical white streaks of surface preparation. Photograph by Christopher Antkowiak.

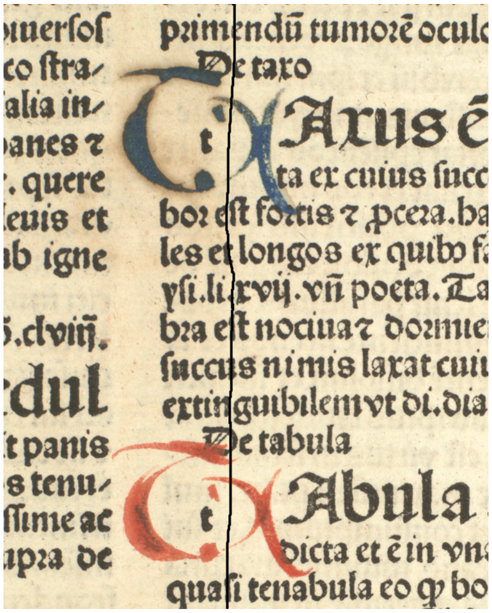

Fig. 18. Anglicus, blue initial "T" above a red "T." Bartolomaeus Anglicus. Photograph by Christopher Antkowiak.

Fig. 19. Anglicus fol. A6ᵛ under UV illumination. Photograph by Christopher Antkowiak.

beyond the areas of paint application. UV examination was carried out on all of the incunabula in the survey, but no evidence of similar preparation of paper was observed.

False color infrared photography results for the Anglicus showed that the blue pigment used in the text as well as in the undamaged illuminated initial letter was consistent with the results for blue copper pigments.

SEM-EDX Analysis of Anglicus

Through SEM-EDX the preliminary identification of the pigment as azurite was confirmed, and alum was also detected. The paint layer showed major amounts of copper, with traces of other elements and minor amounts of aluminum, potassium, and sulfur. No chlorine was found (fig. 20). Visually, the appearance of the pigment particles was consistent with the crystalline structure of natural ground azurite. The surface of many of the particles appeared pitted (fig. 21). The paper fibers showed copper content in varying degrees, minor to moderate, as well as greater amounts of aluminum, sulfur, and potassium (fig. 22). The sample of unpainted paper taken from the gutter showed only trace amounts of aluminum, sulfur, and potassium (fig. 23). These findings, combined with the information obtained through the UV examination, confirm that alum was selectively brushed

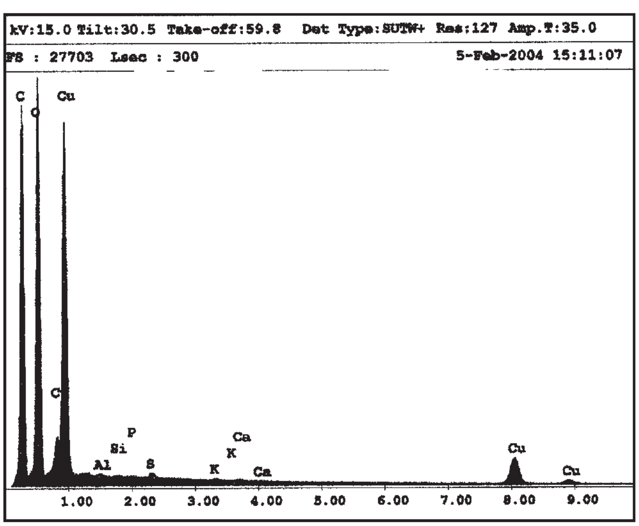

Fig. 20. EDX spectra, Anglicus paint layer.

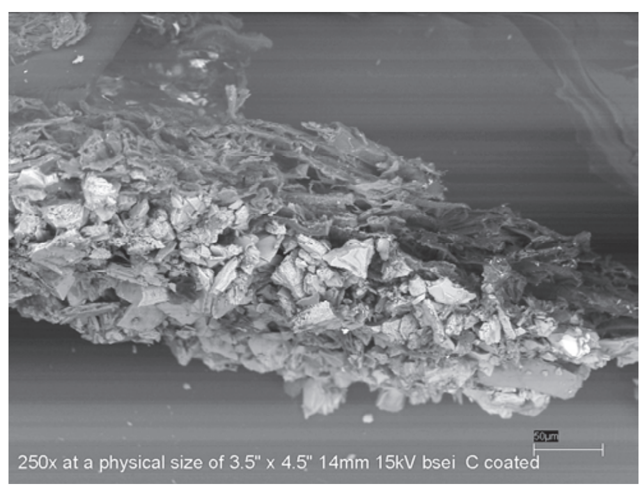

Fig. 21. Scanning electron micrograph, Anglicus. The paint layer (bottom half of sample) shows pigment particle formation characteristic of natural ground azurite.

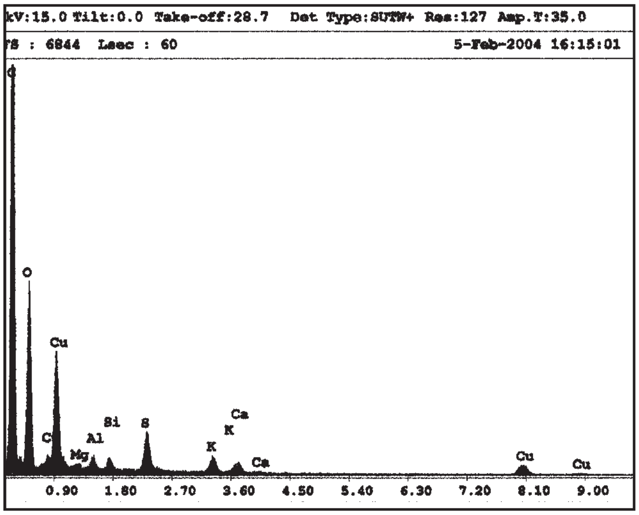

Fig. 22. EDX spectra, Anglicus paper fiber near paint layer.

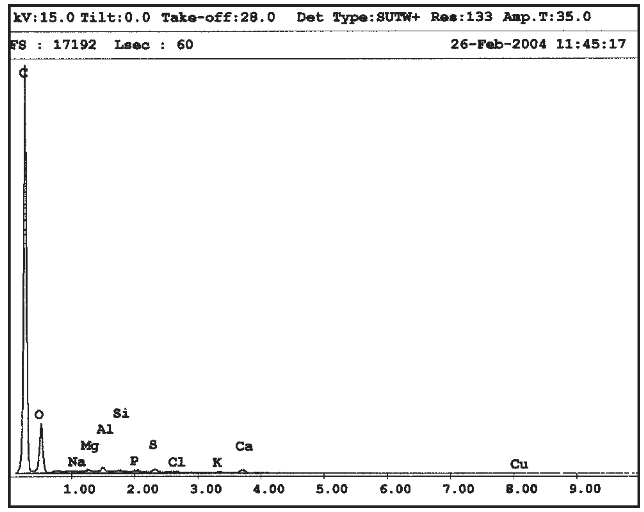

Fig. 23. EDX spectra, Anglicus paper fiber from gutter of bifolium.

onto the paper by the decorator to prepare the surface for painting.

FTIR Analysis of Anglicus

Results for the analysis of the paint layer using FTIR showed that the characteristic carbonate peaks for azurite were present at 3430, 1438, and 867 cm^{-1} (Bruni et al. 2002), confirming the identification of the pigment as a copper carbonate (fig. 24). To broadly characterize the binding medium which had been used, the spectra from the Anglicus sample were compared with spectra derived from binding media/azurite mixtures prepared as in the aging tests. It was found that the Anglicus spectra shared the same vibrational frequencies as the spectra of both the glair and the gum arabic/azurite mixtures, indicating that both plant gum and glair are probably present in the sample (fig. 25, table 1). Comparison with spectra obtained from reference samples of azurite in parchment size, gelatin, and tawed goatskin glue showed that a protein glue was not present in the Anglicus sample. In the glair/alum/azurite mixture in figure 25, a peak at 1090 cm^{-1} indicates the presence of sulfate groups from the alum, which can also be seen in the Anglicus sample.

Conservation Treatments

Because such varied reactions to natural materials had been observed in the earlier testing, a test of materials in accelerated aging conditions was undertaken to assist with planning physical stabilization of the Anglicus. Tests of some materials which would not normally be selected in actual treatment situations were included for purposes of comparison. These tests showed good aging results for the commonly-used consolidants gelatin and isinglass. As suggested by the known behavior of copper and acidic polysaccharides, use of funori (a red seaweed mucilage) as a consolidant resulted in discoloration indicating deterio-

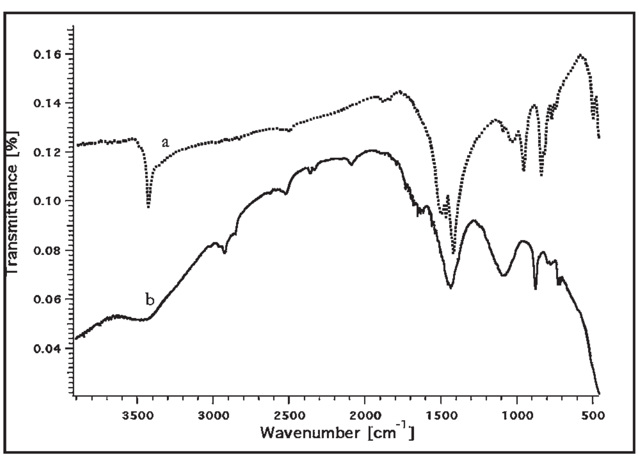

Fig. 24. FTIR spectra of azurite reference sample [a] and Anglicus paint sample [b].

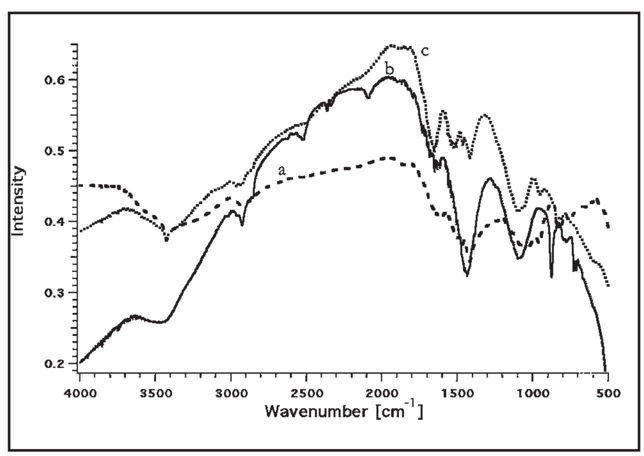

Fig. 25. FTIR specta of azurite in gum Arabic [a], Anglicus paint sample [b], and azurite/alum/glair [c].

ration of cellulose. None of the mending materials caused any discoloration upon aging, and all were easily removed. Isinglass tissue, applied as a remoistenable film, was selected to support the damaged initials because of its working properties and stability in contact with azurite.

Six consolidants were tested on azurite in a gelatin medium: gelatin, parchment size, isinglass, funori, Klucel G/ethanol and Paraloid B-72/acetone. Samples were aged for three days at 50% RH/90°C, consolidants were applied, and aging continued for another eight days. One set duplicated a typical treatment application, applying consolidant in small amounts, pre-wetting with ethanol while working under a microscope. The materials in this group did not show any discoloration. In the other set, a larger brush loaded with consolidant was applied to the paint layer in a single stroke. When this heavy application of the same consolidants was used, only funori caused noticeable discoloration on the verso of the paper support (fig. 26). The natural consolidants from animal sources did not show any discoloration of either the paint layer or the verso, nor did the synthetic adhesives.

Because the gelatin medium had such a protective effect in previous tests, mending materials were tested using more problematic media, so azurite was prepared in gum and glair. Aging was carried out for three days at 50% RH/90°C, mends were applied, and aging continued for eight more days. Mends using wheat starch paste, solvent-set tissue, re-moistenable methyl cellulose tissue, and re-moistenable isinglass tissue were applied to the pigment layer on one half of each sample, and to the paper support on the other half using a minimum of moisture in all cases.

No discoloration was observed in relation to any of the mending materials in this set of tests. In selecting an adhesive for supporting the damaged areas in the Anglicus, avoiding moisture was an important consideration. The re-moistenable isinglass tissue could be applied with minimal moisture[3], and also had the advantage of using an adhesive with a history of successful natural aging, from a family which had shown stability in contact with azurite in the previous tests.

All of the mends were removed after aging. This was accomplished easily in all cases by moistening or alcohol-wetting the repair tissue. During removal, the isinglass film was seen to function as a barrier, preventing wetting out of the sample support, while quickly releasing from it.

V. CONCLUSIONS

All of the blue pigment seen in a group of early printed books is consistent with the results for blue copper pigments in tests using false color infrared photography. Discoloration indicating degradation of cellulose has been observed in half of these examples. Analysis using SEM-EDX and FTIR has shown that the blue pigment used in

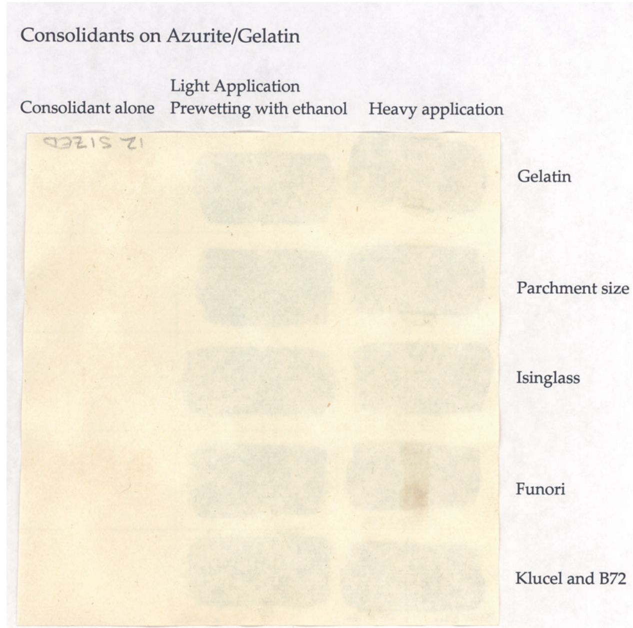

Fig. 26. Verso of consolidant sample sheet, showing staining caused by brush stroke of funori applied to azurite paint layer on recto of sheet.

the rubrication of a severely deteriorated example is natural azurite, and that alum is also present in the surface preparation of the paper by the decorator. It is likely that the embrittlement is the result of alum and azurite reacting to degrade cellulose, a finding which is consistent with other reported examples. FTIR analysis also indicates that the binding medium is probably a gum-glair mixture, and therefore the effective complexing of copper with gum arabic, documented in other studies, may also have contributed to the deterioration in this example. In considering possible treatments of this item, gelatin and isinglass demonstrated favorable results as consolidants in accelerated aging tests. All of the mending adhesives performed well in these tests, and isinglass tissue was preferred for its particular working properties. Aging test results for funori indicate that its use as a consolidant for copper-containing pigments should be avoided.

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SOURCES OF MATERIALS

Azurite #10250
Gum arabic
Paraloid B-72 (ethyl methacrylate copolymer)
Kremer Pigmente
228 Elizabeth Street
New York, NY 10012

Aytex-P wheat starch
Photogelatin (type B gelatin, 220–250 bloom)
Funori (gloiopeltis mucilage)
Salianski isinglass sturgeon glue
Klucel G (hydroxypropylcellulose)
Marvel Seal 360 (aluminized nylon and polyethylene barrier film)
University of Iowa BH (all hemp) paper
Hewit alum tawed goatskin
Cowley goat and calf vellum
Talas
20 West 20th Street
5th Floor
New York, NY 10011

Usu Mino (handmade kozo paper)
Haini (machine made kozo paper)
Hiromi Paper International
2525 Michigan Avenue
Bergamot Station #G9
Santa Monica, CA 90404

Methyl cellulose (400C)
Sigma-Aldrich
P.O. Box 14508
St. Louis, MO 63178

Rhoplex AC33
Rhoplex AC73 (acrylic resin dispersions)
Conservator's Emporium
100 Standing Rock Circle
Reno, NV 89511

AR-5 Processing for EIR film
Precision Photo & Imaging, Inc.
5758 N. Webster St
Dayton, OH 45414
937-898-7450

NOTES

1. While "rubrication" can indicate markings in red, for the purposes of this discussion this term will be used to denote hand-application of initials, underlining, paragraph marks, and initial-strokes in any color.

2. These five volumes are the Columbia Rare Book and Manuscript Library's copies of Goff A722, Angelus de Clavasio, *Summa angelica de casibus conscientiae.* Nuremberg: Anton Koberger, 10 Feb. 1492; Goff A383, Alexander de Ales, *Summa universae theologiae (Partes I–IV).* Nuremberg, Anton Koberger, 1481–82.

3. The author is grateful to Yana Van Dyke for a helpful discussion of the benefits of various mending materials.

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